

BIOMATERIALS

UDC 666.266.6:616.314-77

MATERIALS FOR DENTAL PROSTHETICS

N. M. Shalukho,¹ M. I. Kuz'menkov,^{1,3} and I. A. Bogdanovich²

Translated from *Steklo i Keramika*, No. 7, pp. 33–36, July, 2012.

The characteristics of dental materials of diverse nature are briefly described and their advantages and disadvantages are analyzed. A promising direction in dental materials science is development of silicate materials, which have gained increasingly wider popularity and recognition in the last few years. Such materials are used to fabricate dental prostheses from monolithic blanks and by layer-wise deposition of their fine powders on metallic substrates.

Key words: metal, alloy, plastic, silicate materials, glass ceramic, dental prosthesis.

The materials used in dentistry are divided into three basic groups: metals, plastics and silicate materials, which alone or in combination with another material comprise a quite wide spectrum of restorative dental materials, each group having definite advantages and disadvantages.

Metals and alloys. These materials make it possible to develop precise and at the same time complex prosthetic structures possessing high mechanical strength under variable loads. Several types of metals and alloys based on them are used in modern dentistry: Co, Cr, Ni, Au, Ag, Ti, Pd, Pt and others. In addition, low cost and therefore wide accessibility should be added to the advantages of non-precious metals and alloys based on them.

A disadvantage of metals is their low aesthetic appeal and the allergenicity of some of them, as a result of which other materials have been used for the last few years [1].

Predominately precious metals are used in dentistry at the present time. Other metals, such as Co, Ni, Cr and Ti, are used to make alloys, called metal-ceramic and glass-crystalline (glass-ceramic), for dental prostheses.

Plastics. Dental plastics with a polyacrylate base, which have appeared in the last few years, have opened a new era in prosthetics and have turned out to be an alternative to metals. They can be polymerized in the patient's oral cavity [1], fabricated into very complex shapes and given a natural exterior appearance relatively easily.

The capability of polymers to interact chemically with one another and to form a chemical-mechanical bond with dentine, enamel and other dental substrates gives an advantage to this class of materials over metals and alloys. Other types of polymers are also used for dental prostheses: polymethylmethacrylate, polyethylene and methacrylate, some of which are used in pure form but most are used in combination with other materials.

However, because in time polymers break down as a result of physical and chemical processes occurring in the mouth, the service life of polymer prostheses is comparatively short. Polymers are weaker than metals, so that they can be used only for a limited amount of time and only under small loads.

It has been proposed that inorganic materials — fine powders of quartz and various glasses — can be added to polymer matrices to eliminate these drawbacks. Thus, filled polymers, called composite materials based on dimethylacrylate, have appeared. These composites are characterized by higher chemical stability compared with unfilled polymers and can also be produced in different colors and hues to better mimic natural teeth. With respect to physical properties these materials are close to those of the solid tissues of teeth and can bond with enamel, forming a uniform sealing layer with their solid dental tissues. In addition, they are easily polished and last longer.

At the end of the 1970s it was proposed that quartz aerosol with 0.4 μm particles be used as filler. Such ultrafine filler is incorporated substantially differently into the structure of a composite material, and for this reason such materi-

¹ Educational Institution – Belorussian State Technological University, Minsk, Belarus.

² Baranovich State University, Baranovich, Belarus.

³ E-mail: unibel.chtvm@tut.by.

als are said to be hybrid materials. Even though this was a substantial step in the direction of improving the physical-chemical properties of materials, polymers with all of their inherent drawbacks, first and foremost, their proneness to decomposition and, in consequence, their short service life, remained as the matrix. The latter drawback was the reason why new types of materials free of these drawbacks were sought. Thus, a new class of materials based on an inorganic, predominately silicate, base appeared [1].

Silicate materials. One of the main objectives in developing silicate materials is to obtain compositions that give a better match with tooth enamel, which consists of 96% inorganic and 4% organic material and water. In addition, the inorganic part is comprised mainly of hydroxyapatite $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ [2].

When it first appeared in Europe porcelain was used to make dental prostheses fabricated by casting technology. However, because of the unavoidable shrinkage occurring during drying and firing it is difficult to keep to the prescribed dimensions. Work was begun in parallel on the development of ceramic powder based prostheses pressed or cast under pressure followed by firing and glazing of their surface. For example, a method of obtaining pressed ceramic crowns by deposition on a ceramic framework, obtained beforehand by casting under pressure followed by sintering of one or several layers of dental porcelain, is proposed in [3].

According to [4], a high-strength composition comprising 15 – 70% aluminum silicate, borosilicate glass or a mixture of these glasses and 60 – 85% ceramic material consisting of Y_2O_3 , ZrO_2 or SiO_2 is used to obtain dental prostheses by casting under pressure.

The prostheses produced by this technology possessed quite high strength (ceramics) and were difficult to fabricate in the required shapes and color range (porcelain). Nonetheless, this was a significant step in the development of dental materials science. The disadvantages listed above also inhere in other materials, which were developed in the second half of the 20th century. These include pyroceramics obtained by thermoplastic technology, which yields material with quite high mechanical strength but does not give the required aesthetic qualities — resemblance to natural teeth. Despite the high bending strength, reaching 600 MPa, and high durability it is not widely used because of inadequate aesthetics [1]. Titanium and zirconium ceramics are also used along with corundum, but they have not found wide application in dentistry.

Subsequently, dental materials science started to develop along two directions. The first direction, starting at the middle of the last century, pursued the development of metal ceramic prostheses. In the second direction, starting at the end of the last century, leading foreign firms started work on the development of whole glass-crystalline (glass-ceramic) prostheses from materials obtained by structure-controlled synthesis. For example, the German company Ivoklar Vivadent AG developed a technology for manufacturing blanks of monolithic glass crystalline materials in the system

$\text{K}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{MeO}$ (Me — Ca, Ba, Mg, Sr), from which dental prostheses were fabricated by mechanical processes using a special computer program [5].

Such monolithic prostheses can also be made from other, most diverse composites consisting of, for example, zinc phosphate, polymer cement and glass ionomer [6].

The authors of [7] patented a zirconium dioxide based ceramic composition to be used for dental prostheses. Aluminum, germanium, tin and lanthanide oxides as well as oxide colorant additives, whose content in dental porcelain can reach 15%, were introduced into the mix to improve the sintering of such zirconium ceramic [8].

Compositions and methods of obtaining hydroxyapatite ceramic by the sol-gel method from hydrated calcium nitrate and triethylene phosphate in 2-methoxy ethanol were developed [9].

Monolithic blanks for dental prostheses [10] based on fluorocanasite glass ceramic were obtained. This ceramic consists mainly of crystals of fluorocanasite $\text{Ca}_5\text{K}_{2+x}\text{Na}_{4x}\text{Si}_{12}\text{O}_{30}\text{F}_4$, where $0 < -x < -1$, whose characteristic feature is its chain structure, which gives high fracture toughness and good fracture resistance. Such glasses crystallize via the formation of, initially, CaF_2 crystallites, which play the role of nuclei on whose surface the main crystalline phase subsequently forms.

The authors of [11] patented a glass ceramic and a method to produce it on the basis of lithium disilicate, which imparts high strength to the ceramic. The glasses for glass ceramics were synthesized in the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{CaO}-\text{ZnO}-\text{SrO}-\text{BaO}$ with molar ratio $(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{SrO} + \text{BaO})/(\text{Al}_2\text{O}_3 + \text{ZnO}) \geq 1.3$. In addition, the following can enter into the glass ceramic composition (wt.%): $\text{B}_2\text{O}_3 \leq 4.9$; $\text{F} \leq 1.5$; $\text{MgO} \leq 2$; $\text{Cs}_2\text{O} \leq 5$; $\text{TiO}_2 \leq 2$; $\text{ZrO}_2 \leq 3$; $\text{SnO}_2 \leq 1$; $\text{Sb}_2\text{O}_3 \leq 1$; $\text{Y}_2\text{O}_3 \leq 3$; $\text{CeO}_2 \leq 1$; $\text{Eu}_2\text{O}_3 \leq 1$; $\text{Tb}_4\text{O}_7 \leq 1$; $\text{Nd}_2\text{O}_5 \leq 2$; $\text{Ta}_2\text{O}_5 \leq 2$. Of interest here is the multicomponent nature of this glass ceramic and the quite wide content range of the constituent oxides, which makes it impossible to form a clear picture of the material's properties.

The authors of [12] synthesized in the system $\text{SiO}_2-\text{CaO}-\text{MgO}-\text{P}_2\text{O}_5$ with small additions of Al_2O_3 , B_2O_3 and CaF_2 a glass ceramic whose crystal phases are tricalcium phosphate ($\beta\text{-3CaO} \cdot \text{P}_2\text{O}_5$) and hydroxyapatite.

In the last few years dental prostheses have started to be manufactured from glass-crystalline materials exhibiting biological activity, i.e., with chemical composition close to that of the solid tissue in natural teeth. For example, the authors of [13] obtained bioceramic prostheses in the systems $\text{Na}_2\text{O}-\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ as well as $\text{K}_2\text{O}-\text{MgF}_2-\text{MgO}-\text{SiO}_2$ and the fluorosilicate system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2-\text{F}$.

To increase the chemical stability of monolithic glass ceramic it is recommended that helenite and α -wollastonite be included in the composition of glass-ceramic materials. This

can be accomplished in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ [14]. Such a whole ceramic material is suitable for crowns.

Monolithic ceramic is also obtained by hydrothermal hot pressing of biologically active glass-crystal powder, mixed with distilled water, under pressure 50 MPa at temperatures 100–350°C. Two phases crystallize: $\text{NaCa}_2\text{HSiO}_3$ and $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_4$. A characteristic of this composition is the absence of pores and a uniform distribution of crystal with size to 3 μm . The microhardness of such ceramic is about 3 GPa, compression strength 460 MPa and the fracture toughness $2.5 \pm 0.3 \text{ MPa} \cdot \text{m}^{1/2}$, which is five times higher than that of ordinary glass ceramic [15]. Monolithic blanks were subsequently subjected to computer-controlled milling.

Thus, monolithic prostheses meet all the basic requirements for strength, biological compatibility and aesthetics. According to [16], the fabrication technology for such dental materials is based on nanosize metal oxides with particle-size 1–300 nm with hot-pressing at 1200°C. Nanopowder for such purposes is obtained by the sol-gel method or plasma chemical synthesis; ZrO_2 introduced in amounts to 60% to increase strength is especially effective [17].

Monolithic glass-crystal prostheses were also obtained at 1600°C from leucite glass ceramic, corresponding to the stoichiometric composition of leucite comminuted to 4 μm . Glass-ceramic prostheses were fabricated by pressing and sintering in air at 1500°C. The disadvantages of this technology are high glassmaking and powder sintering temperatures [18].

It should be noted that the monolithic dental prostheses obtained are of high quality. They are also expensive because expensive high-tech equipment is required.

REFERENCES

1. E. M. Lacy, "Ceramics in restorative dentistry: Past, present and future," *Klinicheskaya Implantologiya Stomatologiya*, No. 2, pp. 65–70 (1997).
2. J. Reyes-Gasga, et al., "Conductivity in human tooth enamel," *J. Mater. Sci.*, **34**(9), 2183–2188 (1999).
3. Sekino Masato, Ushioda Masaaki, Fujinami Kyoichi, and Iwamoto Osamu, *Method of Producing Ceramic Crowns*, US Pat. No. 6740267; Int. Cl. A 61 C 013/08; Tokuyama Corporation (JP); No. 831709; Application March 29, 2001; published May 25, 2004.
4. Carmen Hofmann Carmen, Ludwig J. Gauckler, Gerhard Bayer Gerhard, E. Martin, Atef Malash, Scharer Peter, Luthy Heinz, Klaus Krumbholz, Wigbert Hauner, Janssen Hansjorg, Janda Ralf; Dentsply DeTrey GmbH (DE), *Dental Prosthesis*, US Pat. No. 6126732; Int. Cl. A 61 C 013/00; No. 310425; Application May 12, 1999; Published October 3, 2000.
5. W. Höland, et al., "Principles and phenomena of bioengineering with glass-ceramics for dental restoration," *J. Eur. Ceram. Soc.*, **27**(2–3), 1521–1526 (2007).
6. Correr L. Sobrinho, et al., "Fracture strength of all-ceramic crowns," *Sci. Mater. Med.*, **9**(10), 555–559 (1998).
7. Hauptmann Holder, Schnogl Robert, and Frank Sybille, *Verwendung von Zirkonoxidkeramiken mit Sinterzusatz zur Herstellung von Zahnersatz*, Application No. 19938143, Germany, Int. Cl. A 61 E 6/02; ESPE Dental AG, No. 19938143.7; Application August 16, 1999; published February 22, 2001.
8. Sekino Masato, Nakagawa Hiroyuki, Iwamoto Osamu, and Ushioda Masaaki, *Dental Porcelain*, US Pat. No. 6187701; Int. Cl. A 61 C 013/083; Tokuyama Corporation (Yamaguchi-ken, JP); No. 321551; Application May 28, 1999; Published February 13, 2001.
9. H. Ming-fa, et al., "Gel-to-ceramic conversion during hydroxyapatite synthesis," *J. Am. Ceram. Soc.*, **84**(9), 2123 (2001).
10. Christopher W. Stokes, Russell J. Hand, Ric Van Noort, "Fluorocane glass-ceramics for dental applications," in: *19th Intern. Congress on Glass, Edinburgh, July 1–6, 2001* [Electronic resource].
11. W. Höland, et al., "Mechanisms of nucleation and crystallization in high strength glass-ceramics," *European J. Glass Sci. Technol. B*, **48**(3), 97–102 (2007).
12. K. Wakasa, et al., "Thermal treatment and crystalline structure in dental cast ceramic materials," *J. Mater. Sci. Mater. Med.*, **3**(2), 235–238 (1992).
13. S. Takehiro, "Bioceramics containing a glass phase," *Kogyo zairyo*, **39**(14), 64–65 (1991).
14. M. Lei, et al., "Crystallization and properties of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ dental glass ceramic," *Huadong ligong daxue xuebao. Ziran kexue ban = J. E. China Univ. Sci. and Technol. Nat. Sci. Ed.*, **31**(1), 92–95 (2005).
15. N. Yamasaki, et al., "Preparation of biologically active glass ceramics with rot-shaped crystals dispersion by hydrothermal hotpressing," *J. Mater. Sci. Lett.*, **11**(4), 233–234 (1992).
16. Margaret E. Greene and Robert Morena, *Potassium Silicate Frits for Coating Metals*, US Pat. No. 6423415; Int. Cl. B 32 B 17/06; Corning Incorporated (Corning, NY), No. 652832; Application August 31, 2000; published July 23, 2002.
17. Thomas Conrad, Gerhard Meyer, Gerhard Meyer, *Mit nanoskaligem Metalloxid-Pulver dotierte Leucit-Glaskeramik*, Application No. 1061717 Germany; Int. Cl. A 61 K 6/06; No. 20021061717; Chemichl AG Vaduz; Application December 30, 2002; published July 15, 2004.
18. B. Zhang, "A new technology of microcrystallizing leucite to reinforce dental glass ceramics," *J. Wuhan Univ. Technol. Mater. Sci. Ed.*, **19**(1), 94–95 (2004).